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A STUDY OF THE PART PLAYED BY MIGRATION [OF SUBSTANCE] IN CATALYSIS  
ON POROUS CONTACTS

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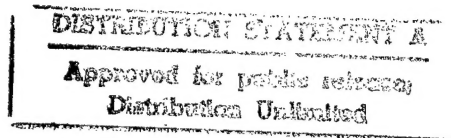
(Translated from  
Izv. Akad. Nauk SSSR, Div. of Chem. Sciences, 1950, 6, 576-581.

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E.R. Hope

Vol. 6: 576-581 (1951)

NAVY RESEARCH SECTION  
SCIENCE DIVISION  
REFERENCE DEPARTMENT



MAY 7-1952

Defence/Scientific Information Service  
(DRB Canada)  
February 21, 1952.

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A STUDY OF THE PART PLAYED BY MIGRATION OF SUBSTANCE  
IN CATALYSIS ON POROUS CONTACTS \*

E.A. ROITER (Reuther)

It is established that for porous contacts the concentration of the reagents in the interior of the crystal is, because of impeded diffusion, always different from the over-all volume concentration. A kinetic equation taking diffusion into account is derived.

In recent years the theory of the kinetics of processes taking place on porous catalysts has undergone a considerable development as a result of papers by Soviet research workers {1-6}. In the papers mentioned, a good deal of attention was devoted to the part played by phenomena of migration of substance and transfer of heat. And indeed we have observed that the rôle of these phenomena is generally underestimated by workers in the field of catalysis, both in research and in practice. What has hitherto been considered as normal is a purely kinetic reaction-course, distorted only under unfavorable circumstances by diffusion. This approach is to be explained by a lack, in research work, of experimental methods which would permit experimental data and theoretical concepts to be used quantitatively to distinguish between the parts played by microkinetic and macrokinetic factors in actual processes.

In our laboratory, two experimental methods have been proposed and worked out for investigating catalytic processes on porous catalysts, methods which make it possible to reveal the part played by macrokinetic factors in catalysis, to study quantitatively and eliminate their distorting effect on the real kinetics of the process.

One of these methods, the "method of separate granules" {7} worked out by M. Rusov et al., consists in studying the speed of the process, in relation to temperature, concentration and other parameters, on separate catalyst-granules of identical geometric shape but of different sizes, freely suspended in a stream of gas. The second

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\* Paper read at joint session of the visiting Division of Chemical Sciences of the Academy of Sciences, USSR, and the Divisions of Physicomathematical and Chemical Sciences of the Academy of Sciences of the Ukrainian SSR, at Kiev, June 9-12, 1950.

is the diaphragm method worked out in cooperation with G.Korneichuk, M.Leperson and N.Stukanovskaya {8}; it consists in investigating the processes on a laminar diaphragm of the catalyst, which divides the reaction vessel into two parts, and over each side of which independent streams of gas may be passed. The pressure on both sides of the diaphragm is kept constant, and exchange between the two parts of the reaction-vessel is possible only by way of diffusion through the catalyst. Paper {8} gave the findings of research, by the diaphragm method, on the process of acetylene oxidation. Since then, researches on other reactions have been carried out.

In every case it was discovered that a marked diminution of concentration is to be observed from the periphery toward the center of the catalyst body, even at very low reaction-velocities. Thus the purely kinetic regime, in which the concentration within the pores and on the surface would have to be identical, is not realized. Naturally the question arises: How far is it possible to depart from the ideal equality of concentration within the catalyst body without incurring a significant error in using the ordinary kinetic equations, which take no account of macrokinetic \* factors? Even a qualitative examination of this question shows that the answer will depend to a considerable extent on the type of kinetic equation. Indeed in the case, for instance, of a reaction of order zero, a wide range of decreases in the internal concentration may exist without causing any decrease in the rate, and therefore the usual kinetic equations will satisfactorily reflect the course of the process right up to the transition into the "Zel'dovich region". But as the order of the reaction becomes higher, the fall in concentration from the periphery to the center of the catalyst body will more and more affect the speed of the process, and the range within which the usual kinetic equations apply will become more and more restricted.

A simple quantitative analysis of the limitations of the kinetic regimes for various types of reaction may be made by taking as our basis the results obtained with the diaphragm method in "closed volume" experiments on these reactions. Two identical streams of the reagent mixture bathe each side of the diaphragm. One of the streams is then shut off, thus creating a closed space, a cul-de-sac, on one side of the diaphragm; on the other side, the gas continues to flow as before. When a steady state has been reached, the gas concentrations are determined on the stream side ( $C_v$ ) and in the closed volume ( $C_k$ ). Here we have in effect a model of the action of a lump of catalyst with radius equal to the thickness of the diaphragm;  $C_k$

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\* As nearly as the translator can understand, the word "macrokinetic" in this paper seems to refer to non-surface factors, factors only involving such things as concentration in the gas-phase. Thus in many cases no special surface factors (microkinetic" factors) are needed to explain the variations of rate in a pore; they can be explained by variation of the concentration in the gas-phase within the pore, a "macrokinetic" factor.

corresponds to the concentration of the gas in the center of the lump. Thus the diaphragm method makes it possible experimentally to determine values of  $C_k$ , and therewith values of the virtual coefficient of diffusion  $D^*$  {8}, which in turn enables us to derive a simple formula for the yield from a porous catalyst over a wide range of conditions.

For greater generality, we shall derive our equation not for the diaphragm but for  $N$  spherical lumps of catalyst of identical radius  $r$  and volume  $v$ , located in a gaseous stream of mean concentration  $C_0$  and rate of flow  $V_0$ . The equation for the diaphragm may be obtained as a particular case of this more general equation.

Let the equation for the ideal kinetic system be expressed as:---

$$\frac{dc}{dt} = -kf(c),$$

where  $k$  is a specific velocity constant, referred to unit volume of the catalyst. Then the yield from the whole catalyst under the conditions of the endokinetic region is:---

$$W = \frac{dx}{dt} = -kNvVf(c). \quad (1)$$

Let us now consider the yield from an infinitely thin surface layer of the granules, a layer of thickness  $dr$ , within which we may take the concentration  $c$  as constant. Evidently this yield will be:

$$dW = -kNS_0Vf(c)dr, \quad (2)$$

since  $dv = NS_0dr$ , where  $S_0$  is the surface area of each lump.

The amount of reagent expended is made up by gas from outside diffusing inward, and this diffusion is, by Fick's law:

$$dW = -D^*NS_0\frac{d^2c}{dr^2}dr. \quad (3)$$

Equating expressions (2) and (3), we get:---

$$\frac{d^2 c}{dr^2} = \frac{kV}{D^*} f(c) \quad (4)$$

which, upon integration between limits 0 to  $\frac{dc}{dr}$  and  $C_0$  to  $C_k$ , gives:

$$\frac{dc}{dr} = \pm \sqrt{2 \frac{kV}{D^*}} \sqrt{\int_{C_0}^{C_k} f(c) dc} \quad (5)$$

Taking into consideration that the yield on the catalyst is equal to the quantity of gas diffusing inward through the surface of the lump (or of the reaction-products diffusing outward), that is,

$$W = - D^* NS_0 \frac{dc}{dr},$$

we obtain:

$$W = NS_0 \sqrt{2kD^* V} \sqrt{\int_{C_0}^{C_k} f(c) dc} \quad (6)$$

With  $N = 1$ , this same equation (6) applies both to the case of the single lump suspended in the gas stream, and to the case of the diaphragm.

The yield from a cubic centimeter of the catalyst containing  $N$  granules (yield per unit volume,  $W_0$ ) will, if we take into account that in this case  $N = \frac{1}{V}$ , be given by the expression:

$$W_0 = \mp \frac{3}{r} \sqrt{2kD^* V_0} \sqrt{\int_{C_0}^{C_k} f(c) dc} \quad (7)$$

where  $V_0$  is the flow-rate per  $\text{cm}^3$  of the catalyst.

Equations (6) and (7) cover the course of the process throughout the whole region of reaction-velocities within which it is possible to consider diffusion from outside as still present: that is, they cover both the so-called endokinetic and endodiffusive regions, and the transitional region between them.\*

For  $f(c) = c^n$ , equation (7) after integration takes the form:

$$W_0 = \frac{3}{r} \sqrt{\frac{2}{n+1} kD^* V_0} \cdot \sqrt{C_0^{n+1} - C_k^{n+1}} \quad (8)$$

When  $C_k = 0$  (in the "Zel'dovich Region"), this becomes:

$$W_0 = \frac{3}{r} \sqrt{\frac{2}{n+1} kD^* V_0} \cdot C_0^{(n+1)/2} \quad (9)$$

which is the well known Zel'dovich Equation {1}.

For the further analysis of equation (8) and its comparison with the usual kinetic equations, it is convenient to replace  $C_k$  by  $\alpha C_0$ . Equation (8) then takes the form:

$$W_0 = \frac{3}{r} \sqrt{\frac{2}{n+1} kD^* V_0} \cdot \sqrt{1 - \alpha^{n+1}} \cdot C_0^{(n+1)/2} \quad (10)$$

When  $\alpha = 0$ , formula (10) yields Zel'dovich's Equation (9). This Zel'dovich Equation however continues, up to certain point, to describe the kinetics of the process with a sufficient degree of approximation even when  $\alpha$  becomes greater than zero. In Fig. 1 we show a graph of the function  $\sqrt{1 - \alpha^{n+1}}$  for reactions of order 0 to 2.

From the graph it is obvious that the error in using equation (9) instead of the full equation (8) or (10) will not exceed 5% for values of  $\alpha$  as follows:

- \* Endokinetic: where the internal process is kinetically determined.
- Endodiffusive: where the internal process is chiefly determined by diffusion. (Tr.)

for  $n = 0$ ,  $\alpha = 0$  to  $0.1$ ;  
 for  $n = 1$ ,  $\alpha = 0$  to  $0.3$ ;  
 for  $n = 2$ ,  $\alpha = 0$  to  $0.45$ .

Thus the higher the order of the reaction, the farther Zel'dovich's Rule applies in the low temperature direction.

To analyse equation (10) in the neighborhood of the opposite limit, that is, for  $\alpha \rightarrow 1$ , we have to integrate equation (5), converting it to the following form:

$$\frac{d\alpha}{dr} C_0 = \sqrt{\frac{2}{n+1} \frac{kV}{D^*}} \cdot C_0^{(n+1)/2} \cdot \sqrt{1 - \alpha^{n+1}} \quad (11)$$

$$\int_1^\alpha \frac{d\alpha}{\sqrt{1 - \alpha^{n+1}}} = \sqrt{\frac{2}{n+1} \frac{kV}{D^*}} \cdot C_0^{(n-1)/2} \int_0^r dr = r \sqrt{\frac{2}{n+1} \frac{kV}{D^*}} \cdot C_0^{(n-1)/2} \quad (12)$$

For values of  $\alpha$  near to unity, we have:

$$\int_1^\alpha \frac{d\alpha}{\sqrt{1 - \alpha^{n+1}}} \sim \sqrt{1 - \alpha^{n+1}}$$

that is

$$\sqrt{1 - \alpha^{n+1}} \sim r \sqrt{\frac{2}{n+1} \frac{kV}{D^*}} \cdot C_0^{(n-1)/2} \quad (13)$$

With  $n = 0$ , expression (13) is valid over the whole interval from  $\alpha = 1$  to  $\alpha = 0$ . The higher the order of the reaction, the nearer to unity the value of  $\alpha$  must be if equation (13) is not to be too rough an approximation.

From Fig. 2 it is seen that with  $n = 1$  equation (13) is valid within the limits  $\alpha = 1$  to  $\alpha = 0.8$ . With  $n = 1$ , equation (13) ceases even at  $\alpha = 0.98$  to describe the process.

The range of values of  $\alpha$  within which equation (13) is sufficiently correct defines the range within which the kinetic equations are applicable without taking into account the disturbing effects of diffusion. In fact, if in equation (10) we substitute

the value of  $\sqrt{1 - \alpha^{n+1}}$  from (13), we get:

$$W_0 \sim kV_0 C_0^n \quad (14)$$

as an equation defining the purely kinetic region.

Thus although for porous contacts no kinetic region in the literal sense of the term exists, an equation derived for that region may describe the process satisfactorily within a more or less extended range of values of  $\alpha$  in the neighborhood of unity, the limits of this range being strongly dependent on the type of kinetic equation. On a simple kinetic basis, the higher the order of the reaction the narrower the range within which equation (14) is applicable. With  $n = 2$  it is practically impossible to set up an experiment in such a way that macrokinetic factors may be left out of account. The same thing, it seems, is true of reversible reactions or of processes which are inhibited by their reaction-products.

The above analysis shows that when using the ordinary procedure, that is, when we try to set up our experiment so as to reduce the influence of macrofactors as much as possible, we may easily fall into error; this indeed seems to have happened in a good deal of previous work. The most correct procedure would be to use equations (6) or (7) straight, determining  $C_k$  by the diaphragm method. In this way it would be possible to find trustworthy values for the specific velocity constant  $k$  and the activation energy, undistorted by macrokinetic factors, to make clear what kinetic regime is involved in the process, and to come to reasonable conclusions as to means of promoting improving the process.

## CONCLUSIONS

1) Investigation, by the diaphragm method, of a number of catalytic processes on porous contacts has shown that the endo-kinetic region is merely an ideal, limiting kinetic case, which



strictly speaking is not realizable. Equations derived for this region without taking macrokinetic factors into account will approximately describe the actual process at low temperatures, but the range of applicability of these equations will be strongly dependent on the type of kinetic equation (the order of the reaction, etc.) and generally speaking it will not be very wide.

2) Equation (7), the general kinetic equation which we have derived, is applicable to the endokinetic, the transitional and the endodiffusive regions; it may be employed directly and the kinetics of the process studied by the diaphragm method.

3) The ideal state which is most easily realizable in practice and accessible for quantitative study is that of the endodiffusive region (the Zel'dovich region). From a study of the kinetics of the process in this region, it is easy to calculate the corresponding parameters for the endokinetic region too. To assign the regime of the process one or the other of these regions, the most unequivocal method is to examine the process by the diaphragm method.

4) It will be necessary to review, from the standpoint of macrofactors and their effects, the majority of researches on porous contacts in which these effects have not been considered, for indeed a correct allowance for the part played by macrokinetic phenomena will lead to a refinement of our understanding of the reaction mechanism and will point the way to an improved efficiency of catalytic processes under industrial conditions.

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Received July 12, 1950

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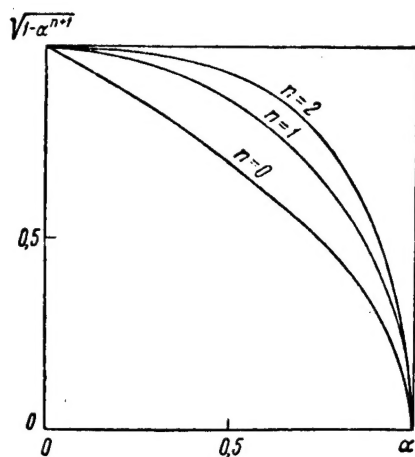


Fig.1. Graphs of the function  $\sqrt{1-\alpha^{n+1}}$  for reactions of different orders.

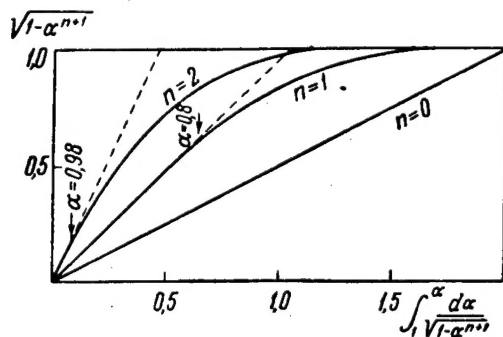


Fig.2. Effect of the order of the reaction on the limits of applicability of equation (13).